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DEPENDENCE OF PORCELAIN WHITENESS ON TECHNOLOGICAL FACTORS AND STRUCTURAL PARTICULARS OF THE MATERIAL

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The interrelations of the properties (whiteness and color) and structure of porcelain and technological factors are examined. The results of the investigation demonstrate the possibility of regulating the whiteness indicators of porcelain by using high-quality raw material, additions of mineralizers, and optimal firing regimes. The use of different methods for determining the whiteness and color of porcelain permits evaluating the effect of technological factors on the formation of the coloristic characteristics of a material. It is determined that the whiteness values determined for porcelain with the Spekol and Pul'sar spectrophotometers could be correlated with one another.

Key words: porcelain, structure of porcelain, methods for evaluating the color and whiteness of porcelain, technological factors, firing temperature, carbon monoxide, coloring oxides.

Whiteness, translucence, and hardness are unique characteristics of porcelain. Human perception of porcelain's color depends on many factors (external illumination, the eye's sensitivity, and others).

The existing method of determining whiteness with the Spekol spectrophotometer at ceramic plants does not always identify the color of porcelain.

Color models used to determine color comprise a collection of absolute or relative color parameters that make it possible to describe color in the color spaced use by means of mathematical description of color in computer technologies [1].

In recent years the $L^*a^*b^*$ color model developed by the International Commission on Illumination (CIE) has been used to determine color and whiteness. In this model color is described by three parameters — luminance and two chromatic components: a^* — varying from green to red and b^* — varying from blue to yellow. The values of the characteristic components a and b are numbers ranging from – 128 to + 128. The luminance ranges from 0 to 100%.

Yu. T. Platov and O. V. Glaskov have used the coloristic CIE $L^*a^*b^*$ system to study structure formation in porcelain — from the preparation of porcelain bodies to the formation of the final porcelain structure during firing.

The values of the color and whiteness coordinates obtained in the course of measurements of the coloristic characteristics of porcelain produced by the Ob'edinenie Gzhel' JSC in the CIE and GOST 2478–2000 systems attest to the effect of technological factors on structure formation and coloristic characteristics of the material.

It is known that the whiteness of porcelain depends on the purity of the raw material used in production, first and foremost, the purity and amount of kaolin introduced into the body. The whitest porcelain articles are those whose body does not contain added clay but rather bentonite is used as a plasticizing additive (4 – 6 wt.%). The whiteness of porcelain decreases if coloring oxides (Fe_2O_3, FeO, TiO_2, MnO_2) and corundum with refraction coefficient 1.760 are present in the body [2]. The dependence of the whiteness of the porcelain from Ob'edinenie Gzhel' on the content of the coloring oxides is presented in Fig. 1.

The whiteness and coloristic characteristics in porcelain samples manufactured by Ob'edinenie Gzhel' are presented in Table 1. The degree of porcelain whiteness can be determined tentatively from the molecular formula (Table 2). For example, on the basis of the content of $Fe_2O_3 + TiO_2$ the lowest value of the whiteness is seen in the sample MR and

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TABLE 1. Results of Whiteness Determination in the Coloristic System $L^*a^*b^*$ and According to GOST 24768–2000

Sample	Porcelain body	Color, whiteness coordinates[1] (CIE)							Whiteness,[2] %, GOST 24768–2000	Firing temperature, °C
		L	a^*	b^*	S	H	G	W_{iso}, %		
1	MR	79.714	– 0.762	3.855	3.930	101.187	8.155	35.533	53	1320
2		81.424	– 1.211	5.739	5.865	101.912	11.594	29.001	47	1340
3		82.623	– 1.573	2.371	2.845	123.359	4.055	49.156	65	1380
4		83.242	– 1.801	2.369	2.976	127.236	3.829	50.409	67	1410
6	GP-2	79.735	– 0.639	3.444	3.503	100.502	7.372	37.783	55	1320
7		84.181	– 1.160	5.538	5.658	101.832	10.929	36.045	52	1340
8		80.592	– 1.452	1.095	1.819	142.966	1.425	51.960	61	1380
9		84.151	– 1.375	1.674	2.166	129.392	2.690	55.819	68	1410
10	MMG	82.734	– 1.483	3.332	3.647	113.992	6.180	44.370	58.5	1320
11		80.858	– 1.280	4.361	4.544	106.353	8.682	35.124	55.1	1380
12		83.618	– 1.970	2.241	2.983	131.324	3.395	51.384	68	1410
13	MKA	84.725	– 1.655	2.748	3.208	121.058	4.698	51.503	67	1320

Notations: L) luminance; a and b) color coordinates; S) degree of saturation; H) hue; G) yellowness; W_{iso}) whiteness.

[1] Determined with the Pul'sar spectrophotometer.

[2] Determined with the Spekol spectrophotometer.

highest in MKA. The results of firing performed in chamber furnaces at 1320°C (the volume content of carbon monoxide in the furnace is about 2%) and the duration is about 44 h, confirm this supposition. For porcelain based on English kaolin (see Table 1, sample No. 13), which contains no titanium oxide), and the weight content of the coloring oxides is 0.63%, the highest degree of whiteness (67%) and high luminance and low yellowness were recorded with Spekol. The lowest luminance (53%) corresponded to the porcelain sample MR (see Table 1, sample No. 1) which contains kaolin from the Prosyanovskoe deposit. The whiteness of porcelain based on secondary quartzes from the Gusevskoe deposit (see Table 1, sample No. 6) was 55%. The porcelain body MMG, to which a mineralizer was added in the form of magnesite from the Satka deposit, had a post-firing whiteness of 58.5% (see Table 1, sample No. 10); a high luminance index and low values of the yellowness were recorded in this sample.

It was established in the course of cross firing that a change of the firing conditions, increasing the temperature to 1380 and 1410°C and increasing to 4 – 5% the CO content in the furnace atmosphere during a reducing period increase the luminance and the whiteness of the porcelain while at the same time decrease the yellowness. The porcelain samples with the indicated compositions after firing in tunnel furnaces for different periods of time (22 h — accelerated at 1410°C and 36 h — at 1380°C) had whiteness values to 67 – 68%. At the same it was determined that an increase of

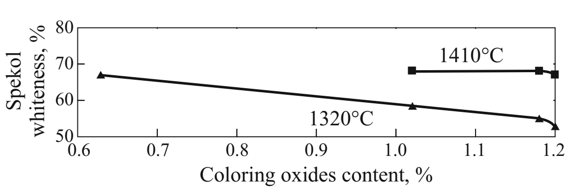

Fig. 1. Porcelain whiteness versus the coloring oxide content. The dots on the curves correspond to the sample numbers in Table 1. The porcelain firing temperature is shown on the curves.

TABLE 2. Molecular Formulas of Porcelain Bodies at Ob'edinenie Gzhel'

Porcelain body	Molecular formula		
MR	$0.152CaO$	$4.24Al_2O_3$	$20.68SiO_2$
	$0.152MgO$	$0.051Fe_2O_3$	$0.120TiO_2$
	$0.547K_2O$		
	$0.168Na_2O$		
MKA	$0.150CaO$	$3.447Al_2O_3$	$17.330SiO_2$
	$0.118MgO$	$0.057Fe_2O_3$	$0.0TiO_2$
	$0.466K_2O$		
	$0.266Na_2O$		
MMG	$0.136CaO$	$2.708Al_2O_3$	$11.005SiO_2$
	$0.487MgO$	$0.033Fe_2O_3$	$0.06TiO_2$
	$0.236K_2O$		
	$0.141Na_2O$		
GP-2	$0.187CaO$	$3.402Al_2O_3$	$15.670SiO_2$
	$0.166MgO$	$0.065Fe_2O_3$	$0.070TiO_2$
	$0.454K_2O$		
	$0.193Na_2O$		

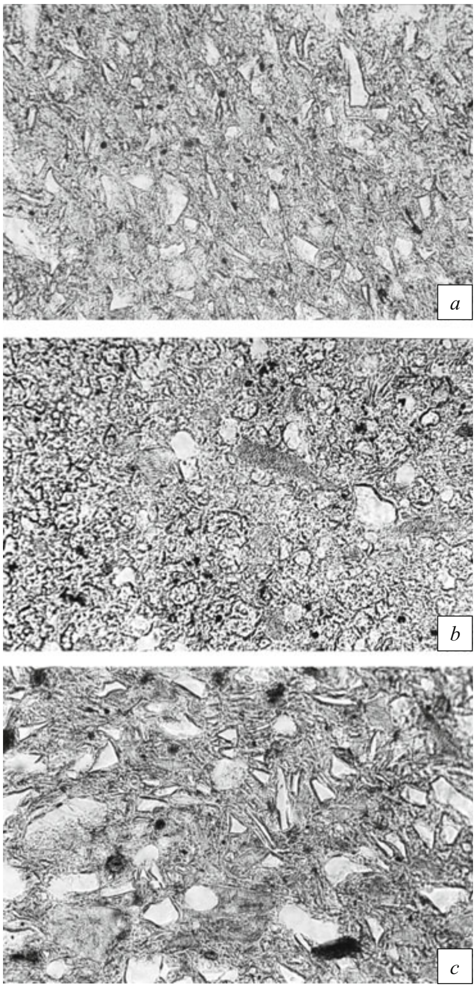

Fig. 2. Structure of porcelain samples from Ob'edinenie Gzhel': *a*) MR; *b*) GP-2; *c*) MMG. Firing temperature 1320°C; × 282.

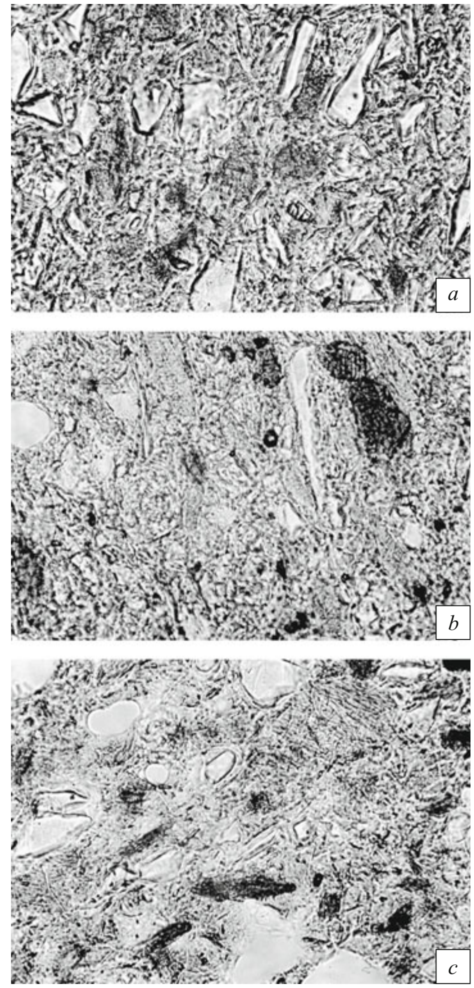

Fig. 3. Structure of porcelain samples from the Ob'edinenie Gzhel': *a*) MR; *b*) GP-2; *c*) MMG. Firing temperature 1410°C; × 564.

the luminance with an increase of the firing temperature was not always accompanied by an increase of the whiteness. For example, the lowest whiteness and highest yellowness were recorded for porcelain samples MR and GP-2 (see Table 1, samples Nos. 2 and 7) fired as 1340°C; this is explained by the firing conditions and the inadequacy of the reducing process during porcelain formation.

Thus, the dependence of the whiteness of porcelain on the content of the coloring oxides in the pastes with low firing temperatures (1320°C) is most clearly established. As the conditions of firing change, the temperature increasing to 1380 – 1410°C and the carbon monoxide content increasing from 2 to 4 – 5%, the effect of coloring oxides on the whiteness becomes less pronounced.

Studies of the structure of porcelains with different whiteness made it possible to classify the porcelain accord-ing the degree of "ripeness." The bodies MR and MMG (Fig. 2*a* and *b*), fired at 1320°C, are insufficiently "ripe." A characteristic feature of the structure of "unripe" porcelain is the negligible edging around quartz grains with the quartz retaining the grain boundaries of feldspars, weakly developed mullite crystals in the form of a network of needles and point accumulations, pores which are mainly small and irregularly shaped, and merging of pores in pockets. The degree of ripeness of porcelain was evaluated on the basis of the structural-mineralogical criteria [3, 4].

As the firing temperature increases to 1410°C, the porcelain structure changes form, acquiring the structural parameters of the normally fired (ripe) porcelain (Fig. 3). Ripe porcelain has the following properties: the developed edging around the feldspar grains 2 – 4 μm, diffuse feldspar grain boundaries, and presence in these regions of a dense network of mullite needles. The mullite in "ripe" porcelain is represented by point formations in the form of fine needles 1 – 2 μm in size.

The presence of grains of incompletely reacted quartz with fragmental structure and distinct elongation was found in the structures of MR and MMG porcelain.

A structural feature of GP-2 porcelain (Fig. 2*b*) based on porcelain stone from the Gusevskoe deposit is represented by

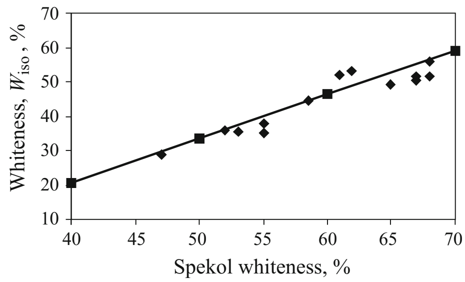

Fig. 4. Correlation curve of the values of the whiteness determined with the Spekol and Pul'sar spectrophotometers: ◆) experimental values of the whiteness; ■) computed values of the whiteness obtained from the equation for a linear polynomial.

an isothermal shape of residual quartz and small grains, 3 – 25 μm in size, which can be explained by the genesis of the quartz present in the kaolinized secondary quartzes (porcelain stone). The GP-2 porcelain structure formed at firing temperature 1320°C is characteristically unripe, the normal degree of ripeness being attained at 1410°C.

A group of scientists [5] determined the main reason for the low luminance of porcelain, associated with inadequate homogenization of the glass-mullite matrix of the material. To obtain a quantitative assessment of the glass-mullite phase, it was proposed that the indicator *Jr*, equal to the ratio of the mullite content to the quart content in the phase composition of the porcelain, which are determined by XPA.

The results of the microscopic studies of porcelain structures with different whiteness confirm the interrelationship between the luminance and the character of the glass-mullite phase. As the firing temperature increases, the luminance indicators are observed to increase in the most samples. Porcelain whose structure has the normal degree of ripeness possesses high luminance with a low value of the yellowness (see Table 1, samples Nos. 3, 4, 9, and 12) and corresponds to normal values of the Spekol whiteness 65 – 68%. In addition, it was established that the luminance and whiteness in samples of GP-2 and MMG porcelain (see Table 1, samples Nos. 8 and 11), whose structure shows indications of scorching and is characterized by an increase of the number of large pores. It was also found that mullitization intensifies when mineralizers in the form of magnesite from the Satka deposit are added to the porcelain composition; this increases the values of the luminance and whiteness of the samples, especially if the firing temperature is low.

To establish the correlation between the whiteness of porcelain as determined on the Spekol and Pul'sar spectrophotometers a statistical model in the form of a linear polynomial was calculated [6]:

$$Y = b_0 + b_1 X;$$
$$Y = 1.282X - 30.63,$$

where $Y = W_{iso}$ is the whiteness in the CIE system; X is the Spekol whiteness, %; $b_0 = -30.63$ and $b_1 = 1.282$ are the computed least-squares coefficients in the regression equation.

This gave a graphical representation of the whiteness in W_{iso} in the CIE system versus the Spekol whiteness (Fig. 4).

TABLE 3. Characteristics of Porcelain Structure

Porcelain body	Firing temperature, °C	Undissolved quartz grains: volume fraction, %	Undissolved quartz grains: width of edging around quartz grains, μm	Undissolved quartz grains: grain shape	Undissolved quartz grains: average length of grains, μm	Pores: volume fraction, %	Pores: average size, μm	Mullite crystal size, μm: at feldspar grain locations	Mullite crystal size, μm: in the overall body
MR	1320	13.8	1 – 2	Fragmental	15.1	6.1	8.8	5 – 7 and 10 – 12	≤ 1
MR	1380	10.5	2 – 3	Fragmental	14.0	6.5	10.6	2 – 6 and 10 – 15	1 – 2
MR	1410	9.1	2 – 4	Fragmental	13.7	6.4	12.4	5 – 10 and 10 – 15	1 – 2
MMG	1320	12.9	1 – 2	Fragmental	18.7	6.4	11.1	5 – 7 and 10 – 12	≤ 1
MMG	1380	9.7	2 – 3	Fragmental	18.1	9.6	17.6	2 – 5 and 10 – 15	1 – 2
MMG	1410	9.6	2 – 4	Fragmental	17.2	7.1	13.6	5 – 7 and 15 – 20	1 – 2
GP-2	1320	10.3	1 – 2	Rounded	11.2	10.3	10.5	2 – 6 and 10 – 12	≤ 1
GP-2	1380	7.0	2 – 3	Rounded	8.9	7.6	11.0	5 – 7 and 10 – 15	1 – 2
GP-2	1410	8.1	2 – 3	Rounded	9.1	8.1	11.2	2 – 10 and 15 – 20	1 – 2

Investigations of the assessment of the quality of porcelain with different compositions showed the presence of an interrelationship between the technological factors, coloristic characteristics, and porcelain structure. To make an accurate identification of the color of porcelain we recommend using different methods of investigation, including the $L^*a^*b^*$ color model developed by the International Commission on Illumination (CIE).

Regulation of the qualitative indicators, such as the whiteness, of porcelain largely depends on the optimal choice of the firing regime and the use of high-quality raw materials with the minimum content of coloring oxides as well as mineralizers which increase the homogenization of the glass-mullite matrix and result in a higher whiteness of the porcelain.

REFERENCES

1. F. Yu. Telegin, *Color in Industry* [Russian translation], Logos, Moscow (2002).
2. I. I. Moroz, M. S. Komskaya, and M. G. Sivchikova, *Handbook of the Porcelain-Earthenware Industry* [in Russian], Legkaya industriya, Moscow (1976).
3. A. M. Batanova and L. S. Bozadzhiev, *Technical Petrography* [in Russian], Izd. MGU, Moscow (1987).
4. A. I. Avgustinik and I. A. Yurchak (eds.), *Investigation and Monitoring Methods in Porcelain and Earthenware Manufacturing*, Legkaya industriya, Moscow (1971).
5. S. Zh. Zhekisheva, N. I. Kudryashov, and G. N. Maslennikova, *Physical–Chemical Aspects of the Technology of Aluminosilicate Ceramics* [in Russian], KRSU, Bishkek (2008).
6. A. G. Bondar', *Mathematical Modeling in Chemical Technology* [in Russian], Vishcha shkola, Kiev (1973).